FINAL REPORT ON...

# WASH WATER SOLIDS

# REMOVAL SYSTEM STUDY

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Prepared For

NASA MANNED SPACECRAFT CENTER

Houston, Texas 77058


DeBELL & RICHARDSON, INC.

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# WASH WATER SOLIDS REMOVAL SYSTEM STUDY

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NASA MANNED SPACECRAFT CENTER
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## SUMMARY

A review of NASA documents shows surfactants to be the most troublesome contaminant for Reverse Osmosis membranes during wash water purification. Surfactants tend to precipitate and foul the RO membranes, causing water flux decline and loss of salt rejection.

A literature search on state-of-the-art techniques uncovered several purification techniques and modifications that appear applicable to an aerospace application.

As a result of concept development feasibility studies, it was discovered that the use of 165 to 190 ppm ferric chloride and optionally 0.25 to 1.0 ppm polymeric flocculant precipitates 92 to 96 percent of the surfactant from an Olive Leaf Soap based wash water.

Crossflow filtration and pressure filtration are promising removal techniques yielding good soap rejection at high water flux rates.

Post-treatment of the chemically pretreated and filtered wash water with activated charcoal removes the residual soap down to an undetectable level (i.e., less than 1 ppm).

Development of specific design criteria and operational parameters will ultimately depend on the choice by NASA of personal hygiene cleansing agent and RO membrane.

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# I. INTRODUCTION

Over the past decade, reverse osmosis has emerged as a convenient and efficient technique for purification of brackish and waste waters. The RO systems are generally compact, the energy requirements are relatively low since the water is not forced through a phase change, and with proper system design it is possible to obtain potable water (i.e., less than 500 ppm NaCl) in a single pass.

With increasingly long space flights taking place and with the possibility of orbiting space stations, it has become necessary for NASA to develop techniques to conserve and reclaim water. Perhaps the single greatest source of contaminated water from such missions will be wash water from bathing and clothes washing. A typical wash water might contain approximately 0.10% soap and 0.5% NaCl; lesser amounts of urea, lactic acid, and phosphate builders; and trace amounts of miscellaneous suspended and colloidal materials such as lint, viruses, bacteria, grease, and soil. It is only natural that NASA would consider membrane separation as a basis for such a development.

Some membrane systems, particularly for reverse osmosis, have been given preliminary evaluation through a joint program by NASA and the Office of Saline Water.

Unfortunately, most of the membranes currently available have been designed primarily for salt rejection, and their operational life is adversely affected by wash water components such as detergents, bacteria, soaps, divalent metal compounds, as well as the 165°F pasturization temperature. Removal of these components in a wash water pretreatment step would improve the operation and life expectancy of the membranes.

The objectives of this program are:

- To determine from the literature which constituent or constituents are contributing to inferior RO membrane performance.

- To develop a preliminary concept for removing the objectionable constituent(s) based on a review of the literature and supporting laboratory feasibility studies.

- To establish design criteria and operational parameters for such a pretreatment system for an aerospace application.

## II. LITERATURE REVIEW - PROBLEM DEFINITION

### SOAP SELECTION

We have conducted a review of the NASA documents reporting the evaluation of various soaps being considered for spacecraft applications. These documents favor Neutrogina and Miranol JEM as personal hygiene cleansing agents (1, 2). Since these agents represent two different classes of surfactants (Neutrogina is an anionic while Miranol is an amphoteric containing both anionic and cationic groups), our concept development work considered both. Olive Leaf soap has also received consideration; because of its simple chemical nature, it was also included as a factor in our development work.

ABS-type detergents (e.g., sodium dodecyl benzene sulfonate) are generally harsh to the skin and are probably not suitable for personal hygiene.

### SYNTHETIC WASH WATER

We have also reviewed the literature in order to determine a typical shower water feed. Table 1 details the results of our survey. The last line of this table is the formulation for the synthetic shower water feed that was used for the concept development work.

The literature indicates the presence of other electrolytes, dissolved organic materials, and suspended solids. The other electrolytes and dissolved organic materials are in relatively low concentration [i.e., magnesium, approximately 35 ppm; calcium, approximately 7.3 ppm (2); and ammonia, 7.0 ppm (4)] ; therefore their absence in our synthetic wash water was not significant to the development work.

Suspended solids, while significant in quantity in real wash water [e.g., 480 ppm (2)] , are a complex mixture of dead skin cells, soil, hair, lint, etc., and would be extremely difficult to duplicate. These materials would likely be removed by prefiltration, either before or after the pretreatment step.

TABLE 1

Wash Water Components
(Parts Per Million)

| Source | Sodium Chloride | Sodium Sulfate | Surfactant | Urea | Lactic Acid | Total Solids | pH |
|---|---|---|---|---|---|---|---|
| A | 568 | 192 | - | - | - | 2800 | 7.7 |
| D | - | - | 1000 | - | - | - | - |
| B | 200 | 30-100 | - | <50 | - | 1600-2000 | 8-8.6 |
| G | 340 | - | 500 | 100 | 75 | 1400 | - |
| E | 2100 | - | 1200 | 1240 | 700 | - | - |
| F | 1500 | - | 10,000 | 1000 | 700 | - | - |
| C | - | - | 1000 | 48 | 83 | - | - |
| D&R | 500 | 150 | 1000 | 50 | 100 | 1800 | 8.0 |

A - Fairchild (shower water analysis) (2)

B - Clemson University (shower water analysis) (4)

C - McDonnell Douglas (theoretical wash water) (5)

D - Chemtric (synthetic shower water) (6)

E - General Electric (synthetic wash water) (7)

F - Envirogenics (synthetic feed) (8)

G - Grumman (synthetic wash water) (9)

D&R - Synthetic Shower Water

## PROBLEM DEFINITION

Contractors who have evaluated reverse osmosis membranes for purification of wash water have experienced various problems.

One problem is fouling by biocides in the wash water. Aerojet-General discovered that hexachloroprene and 4-chloro-3, 5-xylenol caused permanent losses in the water permeability of their membranes (presumably cellulose acetate) (6). Chemtric found that some available RO membranes were unstable in the presence of biocides (10), and that some biocides were not adequately rejected by the membranes.

A more serious problem appears to be that of the soap or detergent. Chemtric found that cationic and anionic species in the water formed sols and/or precipitates which fouled the membranes. Amphoterics tended not to foul, but Miranol solution caused an Eastman membrane to become more pliable (presumably due to plasticization).

Envirogenics conducted twenty one-day storage tests with RO membranes in 1% soap or detergent solutions (8). Exposure to sodium lauryl sulfate and two types of Miranol produced significant decreases in salt rejection of cellulose acetate blend membranes.

General Electric found that Neutrogina and Miranol JEM caused serious (four- to twenty-fold) decreases in water flux through their sulfonated PPO reverse osmosis membranes (11). Olive Leaf soap, among others, had no deleterious effect on flux decline.

Suspended matter was another problem encountered. Envirogenics found that colloidal material caused flux decline, although coarse aggregates appeared to offer no problem (8). Grumman experienced fouling by nonsoluble materials, mainly waxes and oils, but found that prefiltration helped.

Some investigators found that certain organic materials were rejected poorly by the RO membrane. Both Envirogenics (8) and Clemson University (4) experienced poor urea rejection - 36-46% and 5-10%, respectively; and Envirogenics found, in addition, that lactic acid rejection was pH dependent, ranging from 84-98%.

The biocide problem can be overcome by the use of iodine and suspended matter can be removed by filtration. At a recent joint NASA-OSW meeting it was revealed that RO membranes are being modified for improved urea rejection.

From the literature review, however, it is apparent that in order for NASA to be able to keep all of its options open as to choice of cleansing agents and type of reverse osmosis module (i.e., cellulose acetate blend, polybenzimidazole, or General Electric sulfonated polyphenylene oxide), any and all of the surfactant in the wash water feed must be removed prior to the reverse osmosis process.

## III. LITERATURE SEARCH - WATER PURIFICATION TECHNIQUES

We conducted a literature search to uncover various water purification techniques. This search was conducted using Chemical Abstracts from 1960 to the present, as well as miscellaneous publications such as Saline Water Conversion Reports, Desalination, and Desalination Abstracts. The following discusses various purification techniques.

### REVERSE OSMOSIS

Reverse osmosis, or hyperfiltration (12), is a removal technique - a process in which a feed water, generally saline, is passed over the surface of a semipermeable membrane at high velocity and at a pressure sufficient to overcome the difference in osmotic pressures between the feed and effluent sides of the membrane. The process is commonly used for removing dissolved salts from water, but it is also capable of removing certain dissolved organic materials.

The process is operated at pressures from 400 psig (for brackish water) up to 1500 psig (for sea water). Water flux is generally in the order of 1.0 to 20 $gf^2d$ (gallons of effluent per square foot of membrane area per day), with water recoveries as high as 90%. Salt rejections are typically 90-99%.

The advantages of the process, as we are well aware, are as follows:

1. Fouling due to colloidal matter, precipitated soap, and precipitated mineral scale (calcium sulfate) - particularly if the surface velocity of the feed across the membrane is low. This low velocity is common in a high percentage water recovery system such as the du Pont Permasep Permeator. Also to be included here is fouling by large particles of suspended matter - particularly between fine hollow fibers.

2. Attack by bacteria - particularly troublesome with cellulose acetate membranes (13).

3. Chemical attack such as hydrolysis of cellulose acetate due to extremes of pH (14, 15) and oxidation of Nylon membranes in the presence of chlorine.

4. Creep or compression of the membranes resulting from high pressure and accelerated by elevated temperature. This creep results in rapidly declining water throughputs or fluxes with time (16).

## ULTRAFILTRATION

Ultrafiltration is also a removal technique. The process is used to remove dissolved and suspended materials in fluids, again by circulating the feed over the surface of a selective membrane. Since there is no osmotic pressure with which to contend, operating pressures are generally low (e.g., 50-100 psig). Since the membranes are relatively "open", water fluxes are much higher than for reverse osmosis membranes. Due to a slight porosity on the skin of the membranes, separations usually remove materials from approximately 500 molecular weight upward.

The advantages of the process are ease of operation, low energy requirements, very high water throughputs, and efficiency of removal of high molecular weight dissolved and suspended materials.

The principal limitation of the process is fouling. Due to the high water flux through the membrane, it is easy for concentration polarization to occur, in which a layer of concentrated suspended and precipitated matter forms on the surface of the membrane.

Chemical degradation of the membranes can also occur. Chemtric indicates that Stepanol WA-100 (sodium lauryl sulfate) degraded a Diaflo UM-05 (Amicon) ultrafiltration membrane (6).

## DISTILLATION

The distillation process, also a removal technique, including the various types such as Vapor Reheat distillation (17), multistage flash distillation, and vapor compression distillation, essential involves vaporizing the water by heating and then recondensing the vapor in a pure form, leaving the concentrated brine behind. The process removes essentially all dissolved nonvolatile materials and results in a condensate of high purity.

The advantages of the system are high product purity and high rate of conversion of feed into effluent, resulting in good water conservation.

The principal disadvantage of the process is the tremendous amount of energy required. This is due to the fact that the water is forced through an energy consuming phase change (liquid to gas) which requires 540 cal

per gram. Some of the energy can be recovered, however, by allowing the condensing vapors to preheat the feed water.

Another disadvantage is that volatile organic materials can distill over along with the water. Higher temperatures and prolonged heating can also decompose organics to more volatile compounds

## SEQUESTERING AGENTS

Agents such as sodium hexametaphosphate are used as pretreatment chemicals for hard water. These materials sequester heavy metal ions and cause precipitation. This fine precipitate can then be removed by filtration.

These agents are often used as a pretreatment before reverse osmosis. The agents prevent scale formation on the membranes from such materials as calcium sulfate (18).

## ION EXCHANGE

Ion exchange is a removal technique in which a contaminated feed is passed through beds of finely ground polymer on which there is attached either cationic (e.g., amine group) or anionic (e.g., sulfate groups) species. The ionic groups tie up and remove ionic species from the water. The process removes only dissolved electrolytes.

The advantages of the system are that it is simple and easy to operate, the energy requirements are low, and the product water is of a high quality.

The limitations of the process are that a relatively large quantity of resin is necessary to purify large volumes of water. The resins must also be regenerated from time to time, which requires the use of strong acids and alkalis. Finally, the resins - particularly in the anion-exchange bed - are easily fouled by organics, which results in bacterial growth (19).

## ELECTRODIALYSIS

Electrodialysis, again a separation technique, involves separation of ionic species from water by selective transport between two electrodes (20). Partial separation of the components of the solution is accomplished by placing across the path one or more ion exchange type permselective membranes.

Although a single stage of an electrodialysis unit is capable of only 60% salt rejection at best, several stages connected in series into "stacks" are capable of converting brackish into potable water.

The advantages of electrodialysis are, again, ease of operation, high-purity effluent, and low energy requirements.

The single greatest problem with electrodialysis is fouling. There are different types of fouling with different causes, but they all tend to occur principally on the outside of a membrane stack. This fouling causes decreased water flow and loss of rejection.

- Fouling with $Mg(OH)_2$ and $CaCO_3$. This is generally caused by alkalinity at the cathode and may be overcome by acidification. It can also be caused by polarization near the membrane surface; however, any well designed unit should have turbulent water flow or turbulence promoters to eliminate this phenomenon. In addition, a neutral membrane can be used to replace the outer anion permeable membrane to give less polarization and thus reduce scale formation.

- Fouling by organics. This source of fouling is more significant, particularly to a wash water application. Generally the ion exchange type membranes, like ion exchange resins, are fouled or poisoned by materials such as ionic surfactants, humic acid, phenol, proteins, and organic colloids such as starch, gelatin, and egg albumin.

Another limitation with electrodialysis is membrane deterioration caused by oxidants formed at the anode. This is not a significant problem, however, as it can generally be overcome by operating the unit at less than the limiting voltage and by ensuring proper turbulent flow.

## CHEMICAL OXIDATION

Oxidation must be considered a pretreatment technique. The method consists of oxidizing organic materials, using chemical oxidizing agents, to lower molecular weight aldehydes, organic acids, and carbon dioxide. Oxidizing agents include chlorine, chlorine dioxide, ozone, and even potassium permanganate (19).

Advantages are that organic materials such as surfactants can be oxidized to low molecular weight organic acids which might be rejected by the reverse osmosis membrane without another removal step.

Limitations are the toxicity hazard of storing and using materials such as chlorine and ozone gas, and the fact that the wash water, which is relatively

high in organic matter (e.g., 1000 ppm soap), would likely require large amounts of an oxidant for effective pretreatment.

## BIOLOGICAL OXIDATION

Biological oxidation, as it exists commercially, is simply not practical for this application. The equipment used (e.g., trickling filters, activated sludge digesters, and bioclarators) is bulky and the process tends to be very slow.

Enzymes can, in many instances, be attached to resin powders or cloth and used to treat water passing through the bed. This is still a new technique, however, and a wide variety of enzymes might be needed for wash water.

## GRAVITY-ACTIVATED PROCESSES

For the sake of this discussion, gravity-activated separation processes are lumped together and categorized as not feasible due to zero-G considerations. Typical examples are settling (e.g., sand bedding and lagooning), and flotation and microflotation (21).

## IRRADIATION

Kobayashi, T., et al, indicate that trace amounts of ABS type detergents can be decomposed to organic acids by exposure to UV irradiation (2537A).

The limitations of this technique appear to be the restriction to low detergent levels, and a low decomposition rate (0.75-1.05 ppm/minute) (22).

## MULTIFILTRATION

Multifiltration is again a removal process. It is a step-by-step filtering procedure that removes all suspended material and dissolved organics and inorganics (5). Filters - 30$\mu$, 3$\mu$, and 1$\mu$ - remove the suspended matter, two activated carbon columns in series remove the dissolved organics, and ion exchange columns remove the dissolved inorganics.

The advantages of such a system are simplicity and low energy requirements.

The limitations in our application are numerous:

- The filters would have to be back-flushed or replaced rather frequently, as suspended matter for the wash water runs about 500 ppm.

- The system would require fairly large volumes of charcoal and ion exchange resins to handle the volume of water and the relatively large amount of soluble contaminants - 1800 ppm.

- Activated charcoal columns would have to be either replaced frequently or reactivated by heating in a furnace to drive off the organics. In addition, "granular carbon processes are characterized by slow rates" (23).

- As discussed previously, ion exchange resins must be regenerated with the use of strong alkalies and acids.

## CROSSFLOW FILTRATION

Crossflow filtration is another separation process; water, usually high in suspended solids (e.g., pulp mill effluent) is pumped at high circulation velocity over the surface of a coarse filter media - generally constructed of such materials as 325-mesh screen or Dacron cloth. A filter "cake" builds up which in turn separates the suspended matter from the water (24).

Crossflow filtration is generally carried out at 50-100 psig with a circulation velocity as high as 20 feet per second. On startup and until the cake has been built up, pressure and velocity are kept low (e.g., 20 psig and less than 1 foot per second). Filter aids and/or coagulants are frequently used to keep the suspended matter in large particles and thus ensure a high water flux through the cake.

The advantages of the process are separation of suspended solids at higher than normal water flux with only a slow buildup of filter cake due to the high feed velocity. The filter cake also has the ability to act as an ultrafilter and remove some higher molecular weight dissolved organics.

The principal disadvantages are the need for a startup period, during which the cake builds up; and the need for occasional regeneration.

## ACTIVATED CHARCOAL

Activated carbon processes are, again, for removal. The activated carbon (usually charcoal) adsorbs the organic materials from liquids. The process is generally used for low concentrations of adsorbable molecules in applications such as decolorization of sugar solutions, removal of taste and odor from potable water, and removal of dissolved organics from industrial and municipal waste streams(23).

Activated carbon can be used either in granular form in a filter bed or in a powder form added to the water and removed by filtration or by coagulation and filtration. Filtration through a bed of granular charcoal, however, is generally the method of choice.

Advantages of this system are the simplicity of operation, low energy requirements, and high-quality effluent.

The limitations are:

- The system is generally used for trace contaminants (e.g., 10 ppm of an ABS detergent). Large volumes of organics (e.g., 1000 ppm soap, as in wash water) would likely require large amounts of carbon.

- Due to the heavy load of organics, the carbon, if used in granular bed form, would have to be discarded or regenerated in a furnace fairly frequently.

- Granular carbon processes are characterized by slow rates.

- Any organic materials adsorbed on the granular carbon in a column or bed form a nutrient for bacteria. After a time, bacterial growth can become so strong that bacteria appear in the filtrate in large numbers.

- Some organic materials are only weakly adsorbed and may not be completely removed.

## CENTRIFUGE

Centrifuges are used for removal of suspended matter from water. Commercially, centrifugal force is used as a complement to gravity for settling operations in the areas of water and waste treatment (25).

Various types of centrifuges are available including disc, solid-bowl conveyor, and solid-bowl basket centrifuges. The vortex liquid/particle separator developed by Martin Marietta is similar to a solid-bowl conveyor centrifuge. Suspended solids recovery for these techniques runs as high as 98%.

The only serious limitation to a centrifuge is that it removes only suspended matter.

## FILTRATION

Filtration is a removal technique capable of removing particles from less than a micron in size on up. Typical filters are the cylindrical cartridge type made from pleated membranes, giving large surface areas per unit volume, or regenerable filters.

Regenerable filters or back-flushing filters generally comprise a cone-shaped filter media inside a cylindrical housing. The filtration, as opposed to a crossflow filtering or ultrafiltering system, does not use a recirculating feed but relies on 100% transport of the feed through the filter. Back flushing can be done either by timed sequence or by pressure differential across the filter (indicating excessive plugging and low flow).

Limitations of direct filtration are the need to replace filter cartridges or to back flush periodically and the disadvantage that fine porosity filters offer substantial resistance to fluid flow (26). For example, Albany Engineered Systems, manufacturers of the Broughton line of regenerable filters, claims that operation of a system such as we propose, with the relatively high level of suspended solids, would require as much if not more water for back flushing than could be recovered during filtration.

## CHEMICAL PRECIPITATION

Chemical precipitation (i.e., coagulation and flocculation) is a well-known technique for water purification (27,28). Addition of a few parts per million of inorganic coagulants (e.g., alum or ferric chloride) and polymeric flocculants can coagulate and flocculate suspended mater from turbid water.

The limitations of chemical precipitation are:

- Dosage can be critical and may not allow for variations in feed composition.
- The agents act primarily on suspended matter. Materials such as lactic acid and urea are not likely to be precipitated.
- Most of the polymerics must be handled as solutions of 1% in water or less because of their high solution viscosity (high molecular weight).
- Some of the polymerics have limited storage life - especially as solutions.

# IV. CONCEPT DEVELOPMENT

Concept development work on this program involved the use of relatively simple laboratory models for feasibility studies on various purification techniques. These candidate techniques divide into two groups: chemical pretreatment to remove the surfactant from solution, and removal techniques to separate the precipitated soap from the wash water.

## CHEMICAL PRECIPITATION

We began our development work with an investigation of the most promising pretreatment concept, chemical precipitation. This method involves the use of various coagulants, flocculants, and coagulation aids to remove dissolved organics - particularly soap and suspended matter - out of colloidal dispersion and solution. We have employed the conventional jar technique, running experiments in series to get comparative results.

### Material and Equipment

During the program we used the following materials:

| Material | Manufacturer or Supplier | Material Type |
|---|---|---|
| Miranol JEM concentrate | The Miranol Chemical Co., Inc. | Soap |
| Olive Leaf Soap | Rochester Germicide Company | Soap |
| Neutrogena Bar Soap | Neutrogena | Soap |
| Lactic acid (reagent grade) | J. T. Baker Chemical Company | - |
| Urea (USP) | J. T. Baker Chemical Company | - |
| Sodium chloride | J. T. Baker Chemical Company | - |
| Sodium sulfate (reagent grade | J. T. Baker Chemical Company | - |
| Alum $[Al_2(SO_4)_2]$ (USP) | Matheson, Coleman & Bell | Coagulant |

| Material | Manufacturer or Supplier | Material Type |
|---|---|---|
| Ferric chloride solution | Dow Chemical Company | Coagulant |
| Agent CD-208 | GAF Corporation | Flocculant |
| Veegum K | R. T. Vanderbilt Co., Inc. | Coagulation aid |
| Super-OX | Super Chemical Company | Coagulation aid |
| Reten 425 | Hercules, Inc. | Flocculant |
| Reten 220 | Hercules, Inc. | Flocculant |
| Purifloc C-41 | Dow Chemical Company | Flocculant |
| Purifloc N-20 | Dow Chemical Company | Flocculant |
| Nuchar G190-N | Industrial Chemical Sales Div. of West Virginia Pulp & Paper Company | Adsorbant |

## Procedure

The synthetic wash water feed used for this program was:

| Ingredients | ppm |
|---|---|
| Sodium chloride | 500 |
| Sodium sulfate | 150 |
| Surfactant | 1000 |
| Urea | 50 |
| Lactic acid | 100 |

The jar experiments were conducted in 600 ml beakers using 500 ml of wash water feed. The experiments were fun simultaneously, usually three at a time, in order to give comparative results. The procedure was:

1. The coagulant, either alum or polymeric, was added simultaneously to each beaker (e.g., from test tubes fastened to a rod so that all tubes could be tipped at once) to avoid time lag effects. The reagents were added as dilute solutions in water (i.e., 0.2-1%).

2. Within 30 seconds of the addition of the alum, or ferric chloride, the stirrers were turned on to rapid mix - 100 rpm - for 2 minutes to effect the coagulation.

3. The stirrers were slowed to 30 rpm for the slow mix, 15 minutes, during which time the coagulated material grew into floc particles. Optional flocculants were added at the start of the slow mix.

4. After the slow mix, the stirrers were stopped and the rate of settling was observed for 20 minutes.

5. Total dissolved solids was run on promising experimental samples. A 100 mil aliquot of supernatant from the beakers was pipetted carefully and filtered through No. 1 Whatman filter paper to remove any floc. The aliquot was poured into a tared 250 ml beaker and evaporated to dryness in a 105°C oven (constant weight) for approximately 6-8 hours. Total dissolved solids was calculated from the weight of the water and the weight of the dry solids.

6. Promising samples were also analyzed for residual soap content, either by a UV/methylene blue technique or a chloroform extraction/IR technique.

Evaluation Criteria

The following were used as criteria in evaluating the jar experiments.

1. Size and Rate of Flocculation

   Flocculation was observed during the slow mix and the size and rate of flocculation were rated on a scale of zero (no floc formation) to 5 (large floc formed almost immediately) (see footnotes on Table 2).

2. Rate of Settling

   Although floc could not be removed by a settling technique in the zero-G environment of space, the criteria provides a basis for evaluating relative size and density of the floc. The beakers were rated on a basis of zero (no floc) to 5 (settles out, 99-100%, in less than 2 minutes) (see footnotes on Table 2).

3. Total Dissolved Solids

Total dissolved solids on the pretreated, filtered wash water gave an indirect measure of soap content in the water sample (i.e., total dissolved solids minus theoretical dissolved electrolytes) and what we termed an apparent soap removal.

4. Apparent Soap Removal by UV/Methylene Blue Analysis

This technique was used to determine residual soap contents directly in the pretreated/filtered wash water until interferences were discovered.

The analysis procedure involves forming a chloroform-soluble methylene blue/soap complex. The complex is extracted from the water phase with chloroform, is adjusted to constant volume with more chloroform, and the concentration measured by UV absorption at 654 nm. The methylene blue, uncomplexed, is not chloroform-soluble. Apparently, however, the complex forms slowly if at all at acid pH, giving falsely low apparent soap contents.

Subsequent investigations also revealed that ferric chloride was interfering with the analysis. A control sample of distilled water (no soap) containing 100 ppm $FeCl_3$ indicated a soap content of 43 ppm when run through the soap analysis procedure.

The procedure was eventually dropped in favor of a simpler chloroform extraction/IR technique. For the purpose of this report, soap contents determined by the UV/methylene blue technique will be referred to as "apparent soap content".

5. Apparent Soap Removal by Chloroform Extraction/ IR Technique

When it was discovered that we were getting interferences with the UV/methylene blue analysis technique, we decided to use a chloroform extraction/IR technique for determining soap content from carbonyl absorption at 1710 $cm^{-1}$. Lactic acid and urea are relatively hydrophilic, remain in the water phase during the extraction step, and therefore do not interfere with the analysis. This fact was verified by checking known 100 ppm samples of lactic acid and urea.

Results and Discussion

Initial work using coagulation and flocculation was carried out with a synthetic wash water based on Miranol JEM soap. Miranol fared well in previous soap evaluations and was found to be nonalergenic.

The first series (Table 2) was conducted to determine the optimum dosage of alum necessary to coagulate the soap. Too little alum can fail to adequately destabilize the soap miscelles and yield too fine a floc or no floc at all. Too much alum can restabilize the colloidal soap, preventing coagulation. Initial results were not promising; in most cases no floc was formed.

The optimum dosage at pH 8.0 appears to be in the range of 50-65 ppm. There was not sufficient settling to permit a TDS determination.

In work reported in Table 3 we used the optimum alum dosage in conjunction with a flocculant, Agent CD-208, a cationic polyelectrolyte. Although the flocculation was more effective than with alum alone, total dissolved solids determinations revealed poor soap removal.

Other polymerics, used both alone and with alum, were no more effective in removing Miranol JEM from the wash water (Table 4).

Ferric chloride was also evaluated as a primary coagulant for Miranol JEM based wash water, both alone and in combination with various flocculants. Again, analysis revealed very low levels of soap removal (Table 5).

When Neutrogena bar soap was used as the surfactant in the synthetic wash water, the precipitation results were much more promising. Acidification of the water alone removed an apparent 68% of the soap (see Experiment A-418-2, Table 6). The use of 250 ppm alum (A-1259-5) was also effective, removing an apparent 69% of the soap.

Ferric chloride was also effective in removing Neutrogena from wash water. The optimum dosage of ferric chloride was 180 ppm (Table 7), resulting in an apparent soap removal of 70%. Addition of from 1 to 25 ppm of polymeric flocculants to 150 ppm ferric chloride gave no further improvement in soap removal.

The most promising precipitation results came when Olive Leaf Soap was used as the surfactant in the wash water. Ferric chloride alone removes

an apparent 85-90% of the soap with the optimum dosage in the range of 165-190 ppm ferric chloride (Table 8).

The use of 3-7 ppm of Reten 220, a cationic high molecular weight polyacrylamide (in addition to 170 ppm ferric chloride) gave added improvement to the soap removal with values ranging from 87-98% apparent soap removal (see A-1255-1, -2, and -3; A-1253-1, -2, and -3; and A-450-2).

The use of 0.25-5 ppm Reten 425, an anionic high molecular weight polyacrylamide, in addition to 170 ppm ferric chloride gave no improvement in apparent soap removal, although the values were more consistent - ranging from 86-89%.

In all of this work with Olive Leaf Soap based wash water, the apparent soap removal results tend to be variable from one experiment to the other: compare A-441-4 with A-444-1 and A-448-5 (all 170 ppm); and also compare A-439-1 with A-441-2, A-442-6, and A-449-8. For this reason we began to suspect the accuracy of total dissolved solids as a technique for determining residual soap content.

To obtain more accurate data, we repeated some of the more promising precipitation experiments (Table 9). The residual soap was analyzed by both the UV/methylene blue technique and, later, by the more accurate chloroform extraction/IR technique. The actual soap content analyses reveal that 93-95% of the soap is being removed by this technique.

Alum rather than ferric chloride, in dosages from 2.5 to 450 ppm, appears to be ineffective in coagulating the Olive Leaf Soap (Table 10).

A coagulation series was also run with Nalco 603 (Table 11), presumably a polyethylenimine, as the prime coagulant. The analysis showed good apparent soap removal at 40-60 ppm Nalco 603, but there was no improvement over ferric chloride.

TABLE 2

Chemical Precipitation with Miranol JEM-Based Wash Water
Alum Series

| Experiment Number | Dosage of Alum (ppm) | pH of Wash Water | Flocculation Size and Rate (1) | Settling Rate (2) |
|---|---|---|---|---|
| A-403-3 | 25 | 8.0 | 0 | 0 |
| A-403-4 | 35 | 8.0 | 0 | 0 |
| A-403-2 | 50 | 8.0 | 2 | 2 |
| A-403-6 | 65 | 8.0 | 2 | 2 |
| A-402-2 | 100 | 8.0 | 1 | 1 |
| A-404-1 | 50 | 5.0 | 0 | 0 |
| A-404-3 | 50 | 10.0 | 0 | 0 |

(1) Flocculation - rated on a scale of 0-5:

0 - no floc
1 - slow growth; small floc
2 - slow growth; larger floc than (1)
3 - faster growth
4 - large floc in less than 1 min.
5 - large floc almost immediately.

(2) Settling - rated on a scale of 0-5:

0 - no floc
1 - no settling
2 - very little settling (less than 10%)
3 - 99-100% settled out in 20 min.
4 - 99-100% settled out in 2-3 min.
5 - settles out in less than 2 min.

TABLE 3

Chemical Precipitation with Miranol JEM-Based Wash Water

Alum/Agent CD-208 Series

| Experiment Number | Dosage of Coagulant/Flocculant (ppm) | | Coagulation Aid, Veegum K (ppm) | pH | Flocculation Size and Rate | Settling Rate | Total Dissolved Solids (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|
| | Alum | Agent CD-208 | | | | | | |
| A-405-1 | - | 3 | - | 8.0 | 0 | 0 | - | - |
| A-405-3 | - | 5 | - | 8.0 | 0 | 0 | - | - |
| A-405-2 | - | 25 | - | 8.0 | 0 | 0 | - | - |
| A-405-4 | 50 | 3 | - | 8.0 | 3 | 2 | - | - |
| A-405-1 | 50 | 15 | - | 8.0 | 3 | 3 | | - |
| A-405-6 | 50 | 30 | - | 8.0 | 3 | 3 | | - |
| A-406-3 | 50 | 60 | - | 8.0 | 3 | 3 | | - |
| A-407-1 | 50 | 30 | 100 | 8.0 | 4 | 4 | 1600 | 20 |
| A-407-3 | 50 | 30 | 200 | 8.0 | 4 | 4 | | - |
| A-408-1 | 60 | 30 | 100 | 8.0 | 4 | 4 | - | - |
| A-408-3 | 70 | 30 | 100 | 8.0 | 4 | 4 | - | - |
| A-408-4 | 50 | 30 | 100 | 11.0 | 3 | 3 | - | - |
| A-408-6 | 50 | 30 | 100 | 4.0 | 4 | 4 | 1600 | 20 |
| A-412-1 | 50 | 30 | 100 | 3.0 | 5 | 4 | 1750 | 5 |
| A-412-2 | 50 | 100 | 100 | 3.0 | 5 | 4 | | - |
| A-412-3 | 50 | 500 | 100 | 3.0 | 5 | 4 | 1600 | 20 |
| A-413-2 | 50 | 100 | 500 | 3.0 | 5 | 4 | 1690 | 11 |
| A-413-3 | 50 | 100 | 1000 | 3.0 | 5 | 4 | 1660 | 14 |

TABLE 4

Chemical Precipitation with Miranol JEM-Based Wash Water
Alum/Various Flocculants

| Experiment Number | Dosage of Coagulant/Flocculant | | | | Coagulation Aid, Veegum K (ppm) | Flocculation Size and Rate | Settling Rate | Total Dissolved Solids (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|---|
| | Alum | Polymeric (ppm) | | | | | | | |
| | | Reten 425 | Purifloc C-41 | Reten 220 | | | | | |
| A-410-1 | - | 1 | - | - | - | 0 | 0 | - | - |
| A-410-3 | - | 5 | - | - | - | 0 | 0 | - | - |
| A-410-4 | - | 30 | - | - | - | 0 | 0 | - | - |
| A-411-1 | 50 | 3 | - | - | - | 2 | 2 | - | - |
| A-411-2 | 50 | 15 | - | - | - | 1 | 1 | - | - |
| A-411-3 | 50 | 30 | - | - | - | 1 | 1 | - | - |
| A-414-1 | - | - | 100 | - | - | 0 | 0 | - | - |
| A-414-2 | - | - | 500 | - | - | 0 | 0 | - | - |
| A-414-3 | - | - | 1000 | - | - | 0 | 0 | - | - |
| A-414-3b | 50 | - | 1000 | - | 200 | 3 | 3 | 1680 | 12 |
| A-415-1 | - | - | - | 100 | - | 0 | 0 | - | - |
| A-415-2 | - | - | - | 500 | - | 0 | 0 | - | - |
| A-415-3 | - | - | - | 1000 | - | 0 | 0 | - | - |

TABLE 5

Chemical Precipitation with Miranol JEM-Based Wash Water
Ferric Chloride/Flocculant Series

| Experiment Number | Dosage of Coagulant/Flocculant | | | | Final pH (1) | Flocculation Settling | | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|---|
| | $FeCl_3$ (ppm) | Polymeric (ppm) | | | | Size and Rate | Settling Rate | | |
| | | Agent CD-208 | Reten 425 | Reten 220 | | | | | |
| A-420-1 | 25 | - | - | - | 7.5 | 0 | 0 | - | - |
| A-420-2 | 50 | - | - | - | 6.5 | 2 | 3 | 1720 | 8 |
| A-420-3 | 100 | - | - | - | 4.4 | 1 | 2 | - | - |
| A-421-4 | 50 | 1 | - | - | 6.3 | 2 | 3 | - | - |
| A-421-5 | 50 | 5 | - | - | 6.2 | 3 | 5 | 1657 | 14 |
| A-421-1 | 50 | 15 | - | - | 6.4 | 0 | 0 | - | - |
| A-421-2 | 50 | 30 | - | - | 6.4 | 0 | 0 | - | - |
| A-421-3 | 50 | 60 | - | - | 6.4 | 0 | 0 | - | - |
| A-421-6 | 100 | 15 | - | - | 4.3 | 1 | 1 | - | - |
| A-424-1 | 50 | - | 1 | - | 6.2 | 0 | 0 | - | - |
| A-424-2 | 50 | - | 5 | - | 6.1 | 0 | 0 | - | - |
| A-425-1 | 50 | - | - | 1 | 6.3 | 3 | 5 | 1675 | 13 |
| A-425-2 | 50 | - | - | 5 | 6.3 | 0 | 0 | - | - |
| A-425-3 | 50 | - | - | 25 | 6.3 | 0 | 0 | - | - |

(1) Initial pH was 8.3

TABLE 6

Chemical Precipitation with Neutrogena Based Wash Water
Alum Series

| Experiment Number | Dosage of Coagulant/Flocculant (ppm) | | pH | | Flocculation Size and Rate | Settling Rate | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|
| | Alum | Agent CD-208 | Initial | Final | | | | |
| A-418-1 | 65 | - | 7.9 | - | 0 | 0 | - | - |
| A-418-2 | None | - | 3.0 | - | 4 | Cloudy | 1120 | 68 |
| A-418-3 | None | 30 | 3.0 | - | 4 | 2 | - | - |
| A-1259-1 | 100 | - | 8.1 | 7.5 | 4 | Cloudy | 1254 | 55 |
| A-1259-2 | 150 | - | 8.1 | 7.3 | 5 | 2 | 1339 | 46 |
| A-1259-3 | 200 | - | 8.1 | 7.0 | 5 | 2 | 1147 | 65 |
| A-1259-4 | 225 | - | 8.1 | 7.0 | 5 | 3 | 1142 | 66 |
| A-1259-5 | 250 | - | 8.1 | 5.8 | 5 | 4 | 1108 | 69 |
| A-1259-6 | 275 | - | 8.1 | 4.9 | 5 | 3 | 1156 | 64 |

TABLE 7

Chemical Precipitation with Neutrogena Based Wash Water

Ferric Chloride Series

| Experiment Number | Dosage of Coagulant/Flocculant | | | | Coagulation Aid (ppm) | pH | | Flocculation Size and Rate | Settling Rate | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $FeCl_3$ (ppm) | Polymeric (ppm) | | | | Initial | Final | | | | |
| | | Reten 220 | Reten 425 | Purifloc N-20 | | | | | | | |
| A-430-1 | 100 | - | - | - | - | 7.9 | 6.7 | 5 | Cloudy? | - | - |
| A-1251-1 | 150 | - | - | - | - | - | 6.4 | 5 | Cloudy | - | - |
| A-1254-1 | 160 | - | - | - | - | - | 6.2 | 5 | Cloudy | 1196 | 60 |
| A-1254-2 | 175 | - | - | - | - | - | 5.1 | 5 | 4 | 1142 | 66 |
| A-1251-4 | 180 | - | - | - | - | - | 4.3 | 5 | 3 | 1098 | 70 |
| A-1254-3 | 190 | - | - | - | - | - | 3.7 | 5 | 4 | 1168 | 63 |
| A-1251-2 | 200 | - | - | - | - | - | 3.45 | 5 | 3 | 1160 | 64 |
| A-1251-5 | 216 | - | - | - | - | - | 3.3 | 5 | 4 | 1111 | 69 |
| A-1251-6 | 234 | - | - | - | - | - | 3.2 | 5 | 4 | 1100 | 69 |
| A-1251-3 | 250 | - | - | - | - | - | 3.0 | 5 | 3 | 1156 | 64 |
| A-430-5 | 100 | - | - | - | - | 5.0 | 2.9 | 5 | Cloudy | 1320 | 48 |
| A-430-2 | 100 | - | - | - | - | 3.0 | 2.7 | 5 | Cloudy | - | - |
| A-430-4 | 150 | - | - | - | - | 3.0 | 2.7 | 5 | Cloudy | - | - |
| A-431-1 | 150 | 1 | - | - | - | 7.9 | 4.1 | 5 | 4 | 1120 | 68 |
| A-431-2 | 150 | 5 | - | - | - | 7.9 | 4.1 | 5 | 4 | 1070 | 73 |
| A-431-3 | 150 | 25 | - | - | - | 7.9 | 4.0 | 5 | 4 | 1050 | 75 |
| A-435-1 | 150 | 50 | - | - | - | 7.9 | 4.2 | 5 | 3 | 1090 | 71 |
| A-435-2 | 150 | 25 | - | - | Vee-gum K (50) | 7.9 | 4.2 | 5 | 4 | 1080 | 72 |

. . . Continued .

Table 7 (Continued - 2)

| Experiment Number | Dosage of Coagulant/Flocculant | | | | Coagulation Aid (ppm) | pH | | Flocculation Size and Rate | Settling Rate | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $FeCl_3$ (ppm) | Polymeric (ppm) | | | | Initial | Final | | | | |
| | | Reten 220 | Reten 425 | Plurifloc N-20 | | | | | | | |
| A-435-3 | 150 | 25 | - | - | Vee-gum K (100) | 7.9 | 4.1 | 5 | 5 | 1080 | 72 |
| A-433-1 | 150 | - | 1 | - | - | 7.9 | 4.1 | 5 | 4 | 1090 | 71 |
| A-433-2 | 150 | - | 5 | - | - | 7.9 | 4.1 | 5 | 4 | 1100 | 70 |
| A-433-3 | 150 | - | 25 | - | - | 7.9 | 4.1 | 5 | 4 | 1070 | 73 |
| A-434-1 | 150 | - | - | 1 | - | 7.9 | 4.0 | 5 | 3 | 1130 | 67 |
| A-434-2 | 150 | - | - | 5 | - | 7.9 | 4.0 | 5 | 3 | 1120 | 68 |
| A-434-3 | 150 | - | - | 25 | - | 7.9 | 4.0 | 5 | 5 | 1090 | 71 |
| A-436-1 | 150 | - | - | - | Super-Ox (50) | 7.9 | - | 5 | 3 | 1140 | 66 |
| A-436-2 | - | - | - | - | Super-Ox (50) | 7.9 | - | 0 | 0 | - | - |

TABLE 8

Chemical Precipitation with Olive Leaf Soap Based Wash Water
Ferric Chloride Series

| Experiment Number | Dosage of Coagulant/Flocculant (ppm) | | | Coagulation Aid (ppm) | pH | | Flocculation Size and Rate | Settling Rate | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|---|---|
| | $FeCl_3$ | Polymeric | | | Initial | Final | | | | |
| | | Reten 220 | Reten 425 | | | | | | | |
| A-426-4 | 1 | - | - | - | 7.6 | 7.6 | 0 | 0 | - | - |
| A-426-5 | 10 | - | - | - | 7.6 | 7.4 | 0 | 0 | - | - |
| A-426-1 | 25 | - | - | - | 7.6 | - | 0 | 0 | - | - |
| A-426-2 | 50 | - | - | - | 7.6 | - | 0 | 0 | - | - |
| A-426-3 | 100 | - | - | - | 7.6 | - | 0 | 0 | - | - |
| A-439-3 | 135 | - | - | - | 7.6 | - | 0 | 0 | - | - |
| A-439-2 | 150 | - | - | - | 7.6 | 3.7 | 5 | 3 | 1040 | 76 |
| A-448-1 | 150 | - | - | - | 7.5 | 3.6 | 5 | 3 | 987 | 81 |
| A-449-7 | 160 | - | - | - | 7.5 | 3.5 | 5 | 4 | 967 | 83 |
| A-439-1 | 165 | - | - | - | 7.6 | 3.4 | 5 | 4 | 913 | 89 |
| A-441-4 | 170 | - | - | - | 7.6 | 3.4 | 5 | 3 | 908 | 89 |
| A-444-1 | 170 | - | - | - | 7.6 | 3.4 | 5 | 4 | 958 | 84 |
| A-448-5 | 170 | - | - | - | 7.5 | 3.4 | 5 | 5 | 955 | 85 |
| A-441-1 | 175 | - | - | - | 7.6 | 3.3 | 5 | 5 | 965 | 84 |
| A-439-4 | 180 | - | - | - | 7.6 | 3.3 | 5 | 5 | 899 | 90 |

. . . Continued

Table 8 (Continued - 2)

| Experiment Number | Dosage of Coagulant/Flocculant (ppm) | | | Coagulation Aid (ppm) | pH | | Flocculation Size and Rate | Settling Rate | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|---|---|
| | $FeCl_3$ | Polymeric | | | Initial | Final | | | | |
| | | Reten 220 | Reten 425 | | | | | | | |
| A-440-4 | 180(1) | - | - | - | 7.6 | 3.0 | 5 | 4 | 949 | 85 |
| A-441-2 | 180 | - | - | - | 7.6 | 3.3 | 5 | 5 | 949 | 85 |
| A-442-6 | 180 | - | - | - | 7.6 | 3.3 | 5 | 4 | 949 | 85 |
| A-449-8 | 180 | - | - | - | 7.5 | 3.3 | 5 | 5 | 967 | 83 |
| A-441-3 | 185 | - | - | - | 7.6 | 3.2 | 5 | 5 | 960 | 84 |
| A-439-5 | 190 | - | - | - | 7.6 | 3.2 | 5 | 5 | 904 | 90 |
| A-439-6 | 200 | - | - | - | 7.6 | 3.2 | 5 | Cloudy | - | - |
| A-426-6 | 300 | - | - | - | 7.6 | 2.9 | 2 | Cloudy | - | - |
| A-426-7 | 10 | - | - | - | 3.0 | - | 0 | 0 | - | - |
| A-426-8 | 30 | - | - | - | 3.0 | - | 0 | 0 | - | - |
| A-426-9 | 100 | - | - | - | 3.0 | - | 3 | Floats | 1020 | 78 |
| A-437-1 | 150 | - | - | - | 3.0 | 2.5 | 3 | 4 | 974 | 83 |
| A-440-1 | 150 | - | - | - | 3.0 | 2.5 | 5 | 3 | 972 | 83 |
| A-440-2 | 165 | - | - | - | 3.0 | 2.5 | 5 | 3 | 974 | 83 |
| A-444-2 | 170 | 0.4 | - | - | 7.6 | 3.4 | 5 | 4 | 932 | 87 |
| A-444-3 | 170 | 0.7 | - | - | 7.6 | 3.4 | 5 | 4 | 973 | 83 |
| A-450-1 | 170 | 1 | - | - | 7.5 | 3.4 | 5 | 5 | 924 | 88 |

(1) Added dropwise over 10 minutes

...Continued

Table 8 (Continued - 3)

| Experiment Number | Dosage of Coagulant/Flocculant (ppm) | | | Coagulation Aid (ppm) | pH | | Flocculation Size and Rate | Settling Rate | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|---|---|
| | $FeCl_3$ | Polymeric | | | Initial | Final | | | | |
| | | Reten 220 | Reten 425 | | | | | | | |
| A-1255-1 | 170 | 2.5 | - | - | 7.5 | 3.4 | 5 | 5 | 932 | 87 |
| A-1255-2 | 170 | 3.0 | - | - | 7.5 | 3.4 | 5 | 5 | 928 | 87 |
| A-1253-1 | 170 | 3.0 | - | - | 7.5 | 3.4 | 5 | 5 | 827 | 97 |
| A-1255-3 | 170 | 3.5 | - | - | 7.5 | 3.4 | 5 | 5 | 927 | 87 |
| A-450-2 | 170 | 5 | - | - | 7.5 | 3.4 | 5 | 5 | 902 | 90 |
| A-1253-2 | 170 | 5 | - | - | 7.5 | 3.4 | 5 | 5 | 891 | 91 |
| A-1253-3 | 170 | 7 | - | - | 7.5 | 3.4 | 5 | 5 | 825 | 98 |
| A-450-3 | 170 | 25 | - | - | 7.5 | 3.3 | 5 | 5 | 1051 | 75 |
| A-442-5 | 180 | 0.1 | - | - | 7.6 | 3.2 | 5 | 4 | 927 | 87 |
| A-442-4 | 180 | 0.5 | - | - | 7.6 | 3.2 | 5 | 4 | 923 | 88 |
| A-442-1 | 180 | 1 | - | - | 7.6 | 3.2 | 5 | 4 | 939 | 86 |
| A-442-2 | 180 | 5 | - | - | 7.6 | 3.2 | 5 | 4 | 934 | 87 |
| A-442-3 | 180 | 25 | - | - | 7.6 | 3.2 | 5 | 4 | 956 | 84 |
| A-427-1 | 100 | 1 | - | - | 3.0 | - | 3 | Floats | - | - |
| A-427-2 | 100 | 5 | - | - | 3.0 | - | 3 | Floats | 1030 | 77 |
| A-427-3 | 100 | 25 | - | - | 3.0 | - | 3 | Floats | - | - |
| A-437-2 | 150 | 1 | - | - | 3.0 | 2.5 | 5 | 3 | 956 | 84 |

. . . Continued

Table 8 (Continued - 4)

| Experiment Number | Dosage of Coagulant/Flocculant (ppm) | | | Coagulation Aid (ppm) | pH | | Flocculation Size and Rate | Settling Rate | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|---|---|---|
| | $FeCl_3$ | Polymeric | | | Initial | Final | | | | |
| | | Reten 220 | Reten 425 | | | | | | | |
| A-437-3 | 150 | 5 | - | - | 3.0 | 2.5 | 5 | 3 | 943 | 86 |
| A-446-3 | 170 | - | 0.25 | - | 7.6 | 3.4 | 5 | 4 | 933 | 87 |
| A-446-3 | 170 | - | 0.5 | - | 7.6 | 3.4 | 5 | 4 | 939 | 86 |
| A-446-1 | 170 | - | 1 | - | 7.6 | 3.4 | 5 | 4 | 943 | 86 |
| A-1256-1 | 170 | - | 1 | - | 7.5 | 3.4 | 5 | 3 | 913 | 89 |
| A-1256-2 | 170 | - | 3 | - | 7.5 | 3.4 | 5 | 3 | 927 | 87 |
| A-1256-3 | 170 | - | 5 | - | 7.5 | 3.4 | 5 | 3 | 924 | 88 |
| A-445-1 | 170 | - | - | Nuchar C-190-N (30) | 7.6 | 3.4 | 5 | 4 | 936 | 86 |
| A-445-2 | 180 | - | - | Nuchar C-190-N (30) | 7.6 | 3.4 | 5 | 4 | 934 | 87 |
| A-445-3 | 170 | - | - | Nuchar C-190-N (10) | 7.6 | 3.4 | 5 | 4 | 936 | 86 |

TABLE 9

Repeat of More Promising Precipitation Experiments
With Olife Leaf Soap Based Wash Water

| Experiment Number | Dosage of Coagulant/ Flocculant (ppm) | | | Apparent Soap Content (%) (1) | Apparent Percent Soap Removed (1) | Actual (2) Soap Content (%) | Actual (2) Percent Soap Removed |
|---|---|---|---|---|---|---|---|
| | $FeCl_3$ | Polymeric | | | | | |
| | | Reten 220 | Reten 425 | | | | |
| A-1263-1 | 170 | - | - | 38 | 96.2 | - | - |
| A-1263-2 | 180 | - | - | 20 | 98.0 | - | - |
| A-1263-3 | 190 | - | - | 25 | 97.5 | - | - |
| A-1263-4 | 170 | 3 | - | 33 | 96.7 | - | - |
| A-1263-5 | 170 | 5 | - | 27 | 97.3 | 65 | 93.5 |
| A-1263-6 | 170 | 7 | - | 67 | 93.3 | - | - |
| A-1285-1 | 170 | - | 1 | 18 | 98.2 | 65 | 93.5 |
| A-1285-2 | 170 | - | 0.5 | 18 | 98.2 | - | - |
| A-1285-4 | 170 | - | 0.25 | 16 | 98.4 | 59 | 94.1 |
| A-1285-6 | 170 | - | 0.1 | 19 | 98.1 | - | - |
| A-1285-3 | 180 | - | 0.5 | 15 | 98.5 | 48 | 95.2 |
| A-1285-5 | 180 | - | 0.25 | 22 | 97.8 | - | - |

(1) By UV/methylene blue analysis at 654 nm.

(2) By chloroform/IR analysis for carbonyl at 1710 $cm^{-1}$.

## TABLE 10

Chemical Precipitation with Olive Leaf Soap Based Wash Water
Alum Series

| Experiment Number | Dosage of Alum (ppm) | pH | | Flocculation Size and Rate | Settling Rate | TDS (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|---|---|---|---|
| | | Initial | Final | | | | |
| A-429-1 | 25 | 3.0 | - | 2 | Cloudy | - | - |
| A-429-2 | 50 | 3.0 | - | 2 | Cloudy | - | - |
| A-429-7 | 75 | 3.0 | - | 0 | 0 | - | - |
| A-429-3 | 100 | 3.0 | 2.8 | 2 | Cloudy | 1620 | 18 |
| A-429-4 | 100 | 3.0 | - | 0 | 0 | - | - |
| A-429-5 | 150 | 3.0 | - | 0 | 0 | - | - |
| A-429-6 | 200 | 3.0 | - | 0 | 0 | - | - |
| A-438-1 | 90 | 3.5 | - | 0 | 0 | - | - |
| A-438-2 | 110 | 3.5 | - | 0 | 0 | - | - |
| A-438-3 | 130 | 3.5 | - | 0 | 0 | - | - |
| A-1260-1 | 100 | 7.4 | 6.6 | 0 | 0 | - | - |
| A-1260-2 | 150 | 7.4 | 6.2 | 0 | 0 | - | - |
| A-1260-3 | 200 | 7.4 | 5.3 | 0 | 0 | - | - |
| A-1260-4 | 230 | 7.4 | - | 5 (1) | 0 | - | - |
| A-1260-5 | 260 | 7.4 | - | 5 (1) | 0 | - | - |
| A-1260-6 | 300 | 7.4 | - | 5 (1) | 0 | - | - |
| A-1260-7 | 350 | 7.4 | 3.6 | 0 | 0 | - | - |
| A-1260-8 | 400 | 7.4 | 3.5 | 0 | 0 | - | - |
| A-1260-9 | 450 | 7.4 | 3.5 | 0 | 0 | - | - |

(1) Only partial flocculation

TABLE 11

Coagulation and Flocculation of Olive Leaf Soap Based Wash Water
Nalco 603 Series

| Experiment Number | Dosage - Coagulant/ Flocculant (ppm) | | Flocculation Size and Rate | Settling Rate | Apparent Soap Content, ppm (UV) | Apparent Percent Soap Removed (UV) |
|---|---|---|---|---|---|---|
| | Nalco 603 | Reten 425 | | | | |
| A-1286-1 | 100 | - | 1 | Cloudy | - | - |
| A-1286-6 | 80 | - | 2 | Cloudy | - | - |
| A-1286-5 | 70 | - | 2 | Cloudy | - | - |
| A-1286-3 | 60 | - | 5 | 3 | 91 | 90.9 |
| A-1286-2 | 50 | - | 5 | 3 | 92 | 90.8 |
| A-1286-4 | 40 | - | 1 | 2 | 92 | 90.8 |
| A-1286-7 | 30 | - | 1 | Cloudy | - | - |
| A-1286-8 | 20 | - | 1 | Cloudy | - | - |
| A-1287-1 | 60 | 1 | - | - | 172 | 82.8 |
| A-1287-2 | 60 | 0.5 | - | - | 140 | 86.0 |

## REMOVAL TECHNIQUES

The second portion of the concept development work involved evaluation of various removal techniques. These methods generally involved removal of coagulated/flocculated soap particles from the pretreated wash water using what are basically filtration processes. Unless equipment was already available, we employed simple laboratory prototypes constructed from conventional laboratory equipment. For all of this work we used the most promising surfactant, Olive Leaf Soap.

### Evaluation Criteria

Since most of the techniques basically involved filtration, two important criteria of acceptability are:

1. Water Flux

   It is highly desirable to get as large a volume of water through a unit in as short a time as possible while using low energy and a relatively small filter. High water flux, or throughput, for a filter is therefore very important.

2. Flux Decline

   It is important that the high water flux not decrease significantly with time. High flux decline necessitates frequent regeneration or replacement of filters.

Equally important to good water flux and stability is the effectiveness of removal of the soap particles. Techniques for evaluating soap removal again included total dissolved solids (TDS), UV/methylene blue analysis, and chloroform extraction/IR analysis (see pages 16 and 17 for details on these procedures).

### Ultrafiltration - No Chemical Pretreatment

Ultrafiltration was first evaluated as a removal technique without coagulation and flocculation of the soap. It was felt that if a sufficiently "tight" ultrafiltration membrane were used, the relatively large soap molecules could be removed while at the same time adequate water flux was being maintained.

The materials used were:

- Olive Leaf Soap based wash water.
- Diaflo UM - 10 ultrafiltration membrane - Amicon Corporation.
- Diaflo UM - 2 ultrafiltration membrane - Amicon Corporation.
- Diaflo UM - 05 ultrafiltration membrane - Amicon Corporation.

Ultrafiltration was conduced with a conventional research style closed loop system (Fig. 1). This loop, designed for reverse osmosis, has six test stations, two for tubule or hollow fiber membranes and four for thin, flat film membranes. The major components of the system are a pump, reservoir, surge suppressor, pressure and back pressure regulators, filter, ceramic heating element, cooling coil, stirrer, and temperature regulator.

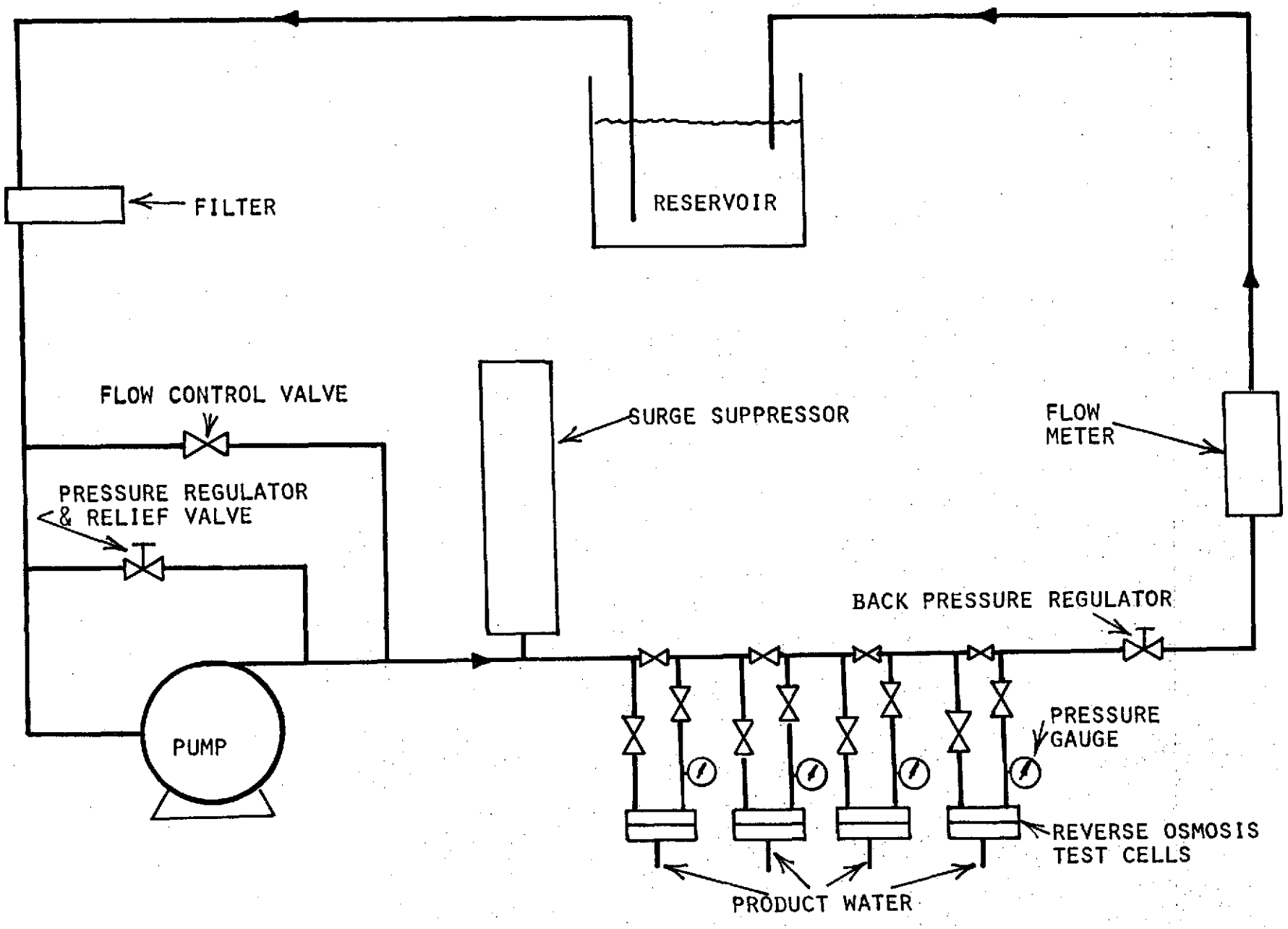
The pump, a Manton-Gaulin Model 125KF3-3BS, has a stainless steel head, is driven by a 5 hp motor, and is rated to deliver 2 gallons per minute flow at 3000 psi pressure. The intake side of the pump is fitted with 3/4-inch polyethylene pipe with a 30-micron Melacel filter (Pall Trinity Micro Corporation) in line. The outlet, high-pressure end of the pump is connected to all 316 stainless steel 3/8-inch tubing. This tubing is a seamless annealed grade suitable for high-pressure use.

Pressure on the output side of the pump is controlled downstream by a Victor Equipment Company Model BRRWQ 8992322 backpressure regulator, dome-loaded with nitrogen pressure from a Model LR 18BB4D4D311 venting type pressure regulator.

The surge suppressor is a 2 foot long, 2 inch diameter pipe with end caps and filled from the top with 200 psig of nitrogen. The surge suppressor is located on the outlet side of the pump, just before the test cells and back-pressure regulator.

As an added safety feature, the outlet side of the pump is equipped with a rupture disc assembly containing a 2355 psig disc. This unit serves to protect the components of the loop from damage in the event of a blockage in the feed flow system. The unit can be set to turn off automatically if the temperature rises or the water level in the hold tank drops.

FIG. 1 - ULTRAFILTRATION TEST LOOP



The reverse osmosis equipment has been modified slightly for the present ultrafiltration work. The Victor venting type regulator (0-2000 psig) was replaced with a Matheson regulator (0-100 psig) for more sensitivity in the low-pressure range. Since the Matheson regulator is not a venting type, a needle valve and tee were installed in the nitrogen line in order to vent the backpressure regulator. A tee and a 0-100 psig gauge were installed in the loop for greater accuracy in measuring pressure. A ball valve was also installed above the tee between the loop and the gauge; this valve can be closed part way to damp out pressure fluctuations to the gauge.

For the ultrafiltration studies we used flat membrane test cells. Membrane discs measuring 2-1/2 inches in diameter are sealed on the perimeter with an O-ring. The feed water passes over the surface of the membrane and permeates through the membrane, a disc of Whatman No. 42 filter paper, a 1/4 inch thick sintered stainless steel disc, and into an effluent collection groove in the bottom flange. Water in this groove exits through an effluent port in the bottom flange of the cell.

The ultrafiltration membrane was first soaked in distilled water and was cut to size using a 2-1/2 inch punch. The wet membrane was placed in the cell, was sealed with an O-ring, and the two flanges of the cell were bolted together. The cell was mounted in the test loop with ferrule fittings.

Olive Leaf based wash water was circulated over the surface of the membranes and pressure was gradually raised to 50 psig using nitrogen pressure against the dome-loaded backpressure regulator. The was water was circulated for a period of several hours at 28-30°C and 60 gallons per hour flow rate.

Samples of effluent were collected at various intervals in tared 250 ml beakers.

Water flux was determined by collecting samples of effluent in tared beakers at various intervals and noting water flux and the decline in water flux with time.

Ultrafiltration of Olive Leaf Soap based wash water using a Diaflo UM-10 membrane lead to the removal of over 50% of the total dissolved solids, most of which was soap (Table 12). The flux decline was severe, however, with a 67% drop in $gf^2d$ (gallons of effluent per square foot of membrane area per day) in only 6 hours. The drop was presumably due to plugging of the surface pores with fatty acid.

The results with the Diaflo UM-2 membrane (Experiment A-1261) were somewhat contradictory. The water flux tended to be lower, which is what would be expected with a tighter membrane (2000 molecular weight cutoff versus 10,000 for UM-10); but the removal of dissolved solids was considerably lower. This may have been due to a flaw in the membrane surface.

Results were somewhat more promising with the Diaflo UM-05 membrane. The water flux, although not especially high, was stable, with little or no drop over a 30-hour period. The total dissolved solids analysis indicates that in addition to essentially all of the soap, presumably some salt and possibly lactic acid were being removed (i.e., the soap represents only 55.5% of the total dissolved solids in the wash water).

The A value in Table 12, known as the intrinsic water permeability, is a parameter commonly used to characterize reverse osmosis membranes. It takes into account operating pressure, membrane surface area, and salt concentration; and gives a measure of the inherent water permeability of the membranes. Typical commercial reverse osmosis membranes have A values of from 0.1 to 1.0 x $10^{-5}$ g/cm$^2$·sec·atm. The inherent water permeability of the UM-05 membrane used in Experiment A-1262 (Table 12) is approximately three orders of magnitude greater than that of a typical RO membrane.

Ultrafiltration of Olive Leaf Soap with a UM-05 membrane shows initial promise, but tests of much longer duration would have to be run to determine if there would eventually be problems with plugging, membrane hydrolysis, etc. The flux for this process was generally low compared to other techniques such as crossflow filtration and pressure filtration.

TABLE 12

Ultrafiltration of an Olive Leaf Soap Based Wash Water[1]

| Experiment Number | Membrane Type[2] | Nominal Molecular Weight Cutoff | Test Duration (hrs) | Water Flux | | TDS (ppm) | Apparent Percent Solids Removed |
|---|---|---|---|---|---|---|---|
| | | | | A x $10^{-2}$[3] | $gf^2d$ | | |
| A-1257 | UM-10 | 10,000 | 1.0 | 2.84 | 21.1 | - | - |
| | | | 2.50 | 2.21 | 16.4 | 855 | 52.5 |
| | | | 4.50 | 1.27 | 9.6 | 796 | 55.8 |
| | | | 6.0 | 0.93 | 6.9 | - | - |
| A-1261 | UM-2 | 2,000 | 1.0 | 0.58 | 4.3 | 1090 | 39.5 |
| | | | 4.0 | 0.44 | 3.3 | 1075 | 30.3 |
| | | | 7.0 | 0.38 | 2.8 | 1173 | 34.8 |
| | | | 25.50 | 0.38 | 2.8 | 914 | 49.3 |
| A-1262 | UM-05 | 500 | 1.0 | 0.84 | 6.3 | 805 | 55.3 |
| | | | 3.75 | 0.90 | 6.7 | 680 | 62.2 |
| | | | 24.50 | 0.73 | 5.5 | 626 | 65.2 |
| | | | 29.50 | 0.78 | 5.8 | - | - |

(1) No chemical pretreatment

(2) Amicon Corporation

(3) Intrinsic water permeability, $g/cm^2 \cdot sec \cdot atm$ (assumes no osmotic pressure).

## Ultrafiltration of Pretreated Wash Water

In initial work we evaluated ultrafiltration as a removal technique using uncoagulated Olive Leaf Soap based wash water. Here we discuss our subsequent evaluation of the ultrafiltration of coagulated and flocculated wash water.

The procedures and equipment were the same as has been previously described, with the following exceptions:

1. There was usually an in-line (30-micron) prefilter for the feed; this was eliminated.

2. The membranes used were Amicon PM-10 and PM-30, with nominal molecular weight cutoff ratings of 10,000 and 30,000. We purposely used fairly open membranes, since this is essentially a filtering operation.

3. The wash water was coagulated and flocculated with 170 ppm $FeCl_3$.

Both membranes were evaluated (separate experiments) at 50 psig. Results are given in Table 13. In both cases the effluent was clear and free of floc, but the fluxes were relatively low, with rapid decline. This rapid flux decline was probably due to plugging of membrane pores with fine particulate matter in the feed.

In general, it appeared that the ultrafiltration was overdesigned for the present application where simple filtration is all that is necessary. It is interesting to compare these results for ultrafiltration with those of cross flow filtration. Despite flux decline, which occurs with both techniques, cross flow tends to give an order of magnitude greater water flux at only 10% of the operating pressure. In addition, cross flow lends itself to regeneration of the filter, while ultrafiltration does not. Based on this assessment, ultrafiltration did not appear satisfactory for the present application and was not given further consideration in the program.

TABLE 13

Ultrafiltration of Coagulated Wash Water

A. PM-30 Membrane - Experiment A-1273

| Time Elapsed (hr) | Flux ($gf^2d$) | Apparent Soap Removal by TDS (%) |
|---|---|---|
| 0.5 | 110.0 | 88.5 |
| 1 | 81.0 | 84.1 |
| 2 | 61.4 | 84.7 |
| 3 | 51.6 | 87.0 |

B. PM-10 Membrane - Experiment A-1275

| | | |
|---|---|---|
| 0.5 | 98.6 | 70.7 |
| 1 | 92.6 | 70.9 |
| 2 | 76.0 | 74.9 |
| 4 | 43.1 | 75.5 |
| 5.5 | 30.0 | 66.2 |
| 7 | 24.1 | 67.3 |
| 9 | 14.2 | 71.6 |

## Crossflow Filtration

Crossflow filtration is a relatively new process developed by G. E. Moore, et al, at Oak Ridge National Laboratory (24). It is similar to RO and ultrafiltration in that the feed is pumped at high velocity over the surface of the filter, but the filter is dynamically formed from filter aids and suspended solids onto a fine mesh screen.

To evaluate crossflow filtration as a removal technique, we constructed a simple laboratory test loop. Fig. 2 is a schematic diagram of the apparatus. The major components are a centrifugal pump (Eastern Industries Model P-7), a pressure gauge (U.S. Gauge, Inc. - 0 to 100 psig), a 5-gallon polyethylene pail to serve as a sump or hold tank, a variable-speed stirrer motor (Gerald K. Heller Company) and blade to agitate the water in the sump, and a membrane test cell of the type used for reverse osmosis. For water lines we used rubber tubing fastened with wire. Thumb-screw style hose clamps were used to help control flow rate and pressure.

The test cell was modified as shown in Fig. 3. Two rubber gaskets, 0.075 inch thick, were placed over the filter to give a deeper space between the filter and the roof of the cell. The filter consists of a 325-mesh screen on top of an 18-mesh screen backing.

In order to prepare a crossflow filter, it is necessary to deposit a thin layer of prefilter on the screen. This was done dynamically by pumping a dilute suspension of filter aid in water over the surface of the screen at low pressure.

For our work we used Solka-Floc BW-20 (Brown Company), a purified wood cellulose fiber, followed by Dicalite 215 (Grefco, Inc.), a porous diatomaceous earth. For a 22-mil thick precoat of Solka-Floc, a dosage of 0.32 ounce per square foot of screen is recommended.

In an initial experiment we used 0.124 g of Solka-Floc BW-20 in approximately 5 liters of water. The Solka-Floc was first predispersed in 50 cc of water using a dispersator with saw-tooth blade to break up aggregates of fiber. The dispersion was pumped over the surface of the screen at approximately 0.5 feet per second and less than 2 psig for one hour. Over the period of one hour, the effluent flux through the screen dropped from 17,960 $gf^2d$ to 7,960 $gf^2d$ as the screen became coated with filter aid.

To examine the cake, the cell was opened and the screen dried in a 60°C air oven. The cake appeared to be eroded away at the entrance port of the

cell as a result of the impact of the high-velocity feed. The cake varied in thickness across the cell from entrance to exit port from essentially 0 mil to 10 mils. To correct for this problem we placed a small aluminum baffle on top of the screen in the area where the entrance water impinged, to absorb the impact and deflect the flow.

In two subsequent experiments (A-1267C and A-1268A) we again attempted to deposit a layer of Solka-Floc, but the rate of flow of effluent through the filter remained fairly constant and there was evidence of breakdown in the cake. To alleviate this problem we tried reducing the cross flow rate. In experiment A-1268-B we started with a cross flow of less than 0.1 ft/sec. The Solka-Floc was added in two aliquots, initially and again at the end of one hour.

The flux through the screen was 3100 $gf^2d$ at the start. During the precoat we gradually raised the cross flow rate and pressure in order to keep the flux in the range of 3000 to 8000 $gf^2d$. At the end of 1-1/4 hours, 0.1 g of Dicalite 215 was added. The final flux was 3000 $gf^2d$ at a cross flow rate of 0.3 ft/sec. The precoat varied in thickness from 7 to 10 mils across the cake.

In experiment A-1269 we ran crossflow filtration on a coagulated and flocculated Olive Leaf Soap based wash water using a screen precoated in the above manner.

Four liters of wash water was flocculated using 180 ppm $FeCl_3$ and a 2-minute rapid mix, followed by a 15-minute slow mix. Flocculation was done in a 5-gallon pail using a variable-speed stirrer.

This flocculated water was used as the feed for crossflow filtration. The feed was stirred rapidly in the sump to keep the floc suspended and was pumped over the surface of the screen at 1.5 ft/sec and 5.5 psig. Over a 45-minute period the flux remained at 1450 $gf^2d$. Total dissolved solids indicated an apparent 80% soap removal, but soap analysis by chloroform extraction/IR would likely have shown greater removal.

In experiment A-1271 the crossflow filtration of coagulated Olive Leaf Soap based wash water was repeated. The filtration was run at 11 psig rather than 5.5 psig; the increase in water flux was not proportional to the increased pressure, however. The pressure was increased 100% while the flow increased only 46%. This diminished flux/psi may have been due to concentration polarization or a greater buildup of the cake due to the higher pressure and resulting higher flux. Analysis by UV/methylene blue indicated apparent residual soap levels in the effluents of between 26 and 63 ppm;

these results are likely in error, as the analyses were done before we discovered a pH sensitivity in the soap analysis procedure.

In experiment A-1290 we determined the effect of filtering to high solids on the ability to pump the sludge and on the decrease in effluent flux.

Table 14 indicates the effect of elapsed time on the decrease in water flux. From 1/4 to 6-1/2 hours the filter was operated at constant suspended solids (approximately 0.12% by weight). From 6-1/2 to 11 hours the water in the sump was allowed to concentrate; a smaller sump was installed to permit a small final volume. During the final 4-1/2 hours, 15,000 cc of coagulated water was reduced to 800 cc, representing a concentration of from 0.12 to 2.2% solids and a 95% water recovery. This experiment did not necessarily establish the upper limit of water recovery; 98-99% is likely. Analysis for residual soap content (the figures may be in error due to pH sensitivity and $FeCl_3$ interference of the soap analysis) reveals a 92% removal of Olive Leaf Soap.

At the end of the experiment the filter was back-flushed by forcing 25 psig water through the effluent port of the cell. Examination of the screen revealed that nearly all of the cake had been removed by this relatively crude back-flushing technique.

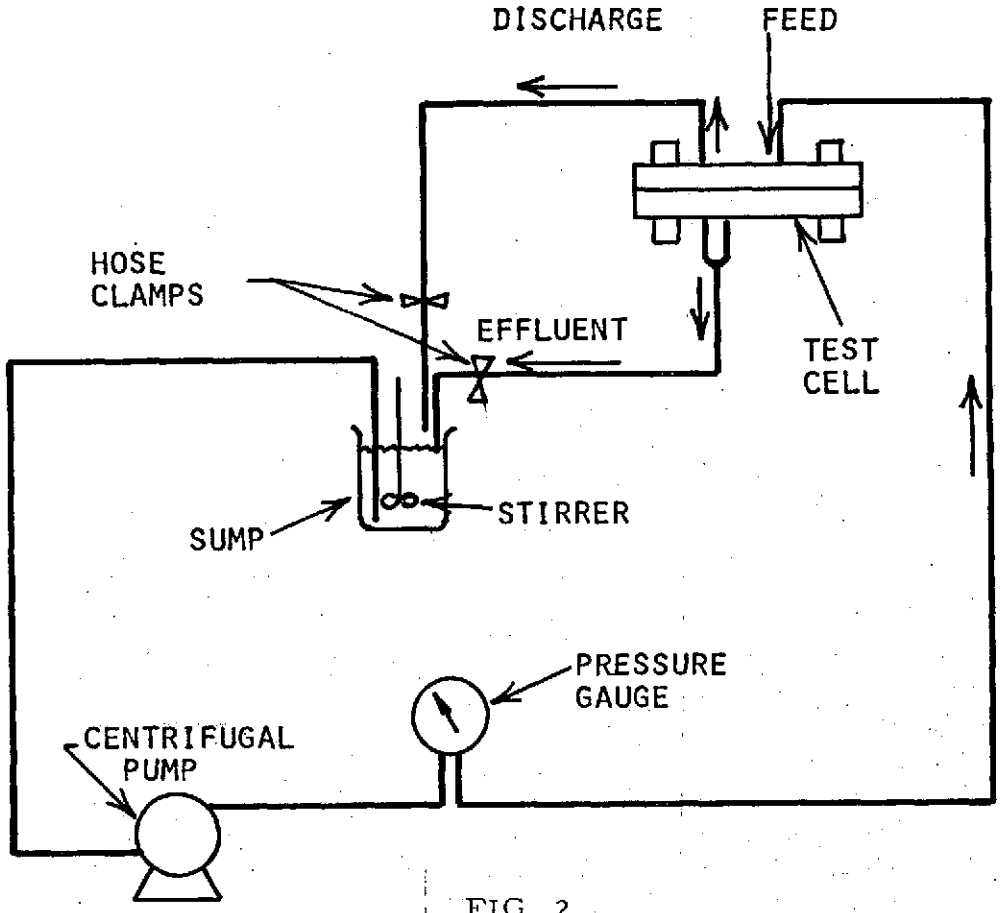



FIG. 2

CROSS FLOW

FILTRATION TEST LOOP

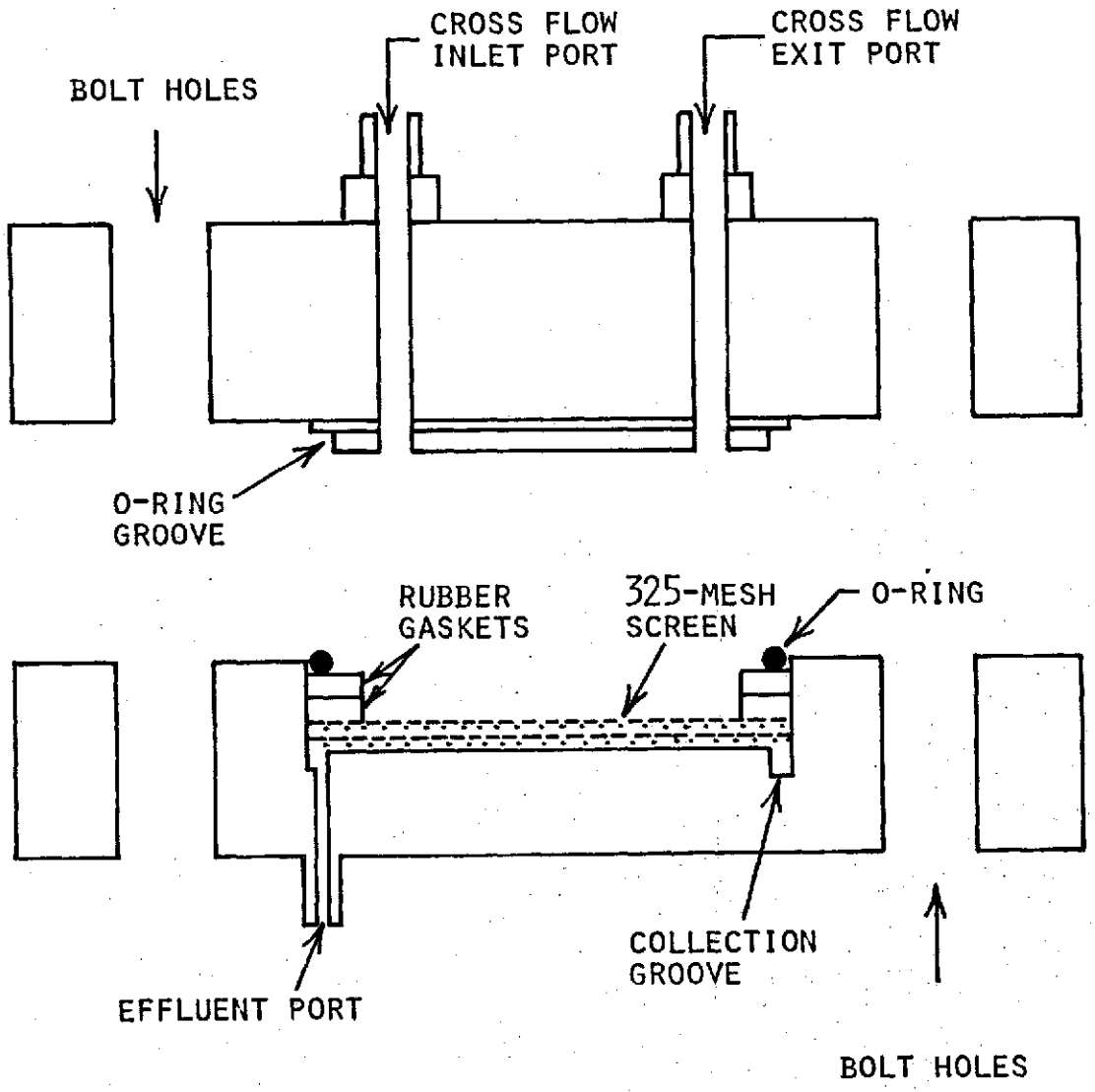



FIG. 3

TEST CELL

TABLE 14

Crossflow Filtration[1] of Coagulated Wash Water[2] to High Solids, A-1290

| Time Elapsed (hr) | Effluent Flux ($gf^2d$) | Apparent Residual Soap (ppm) | Apparent Percent Soap Removed |
|---|---|---|---|
| 0.25 | 1370 | - | - |
| 0.50 | 1220 | 83.9 | 91.6 |
| 1 | 1100 | 68.2 | 93.4 |
| 2.50 | 924 | 79.8 | 92.0 |
| 3 | 780 | - | - |
| 4 | 637 | 85.3 | 91.5 |
| 6.50 | 530 | - | - |
| 7 | 505 | - | - |
| 8 | 460 | - | - |
| 11 | 340 | - | - |

(1) At 5 psig; Solka-Floc BW-20 and Dicalite 215 as filter aids; 325-mesh screen; 1.9 ft/sec crossflow rate.

(2) Olive Leaf Soap based wash water coagulated with 170 ppm $FeCl_3$ and flocculated with 0.25 ppm Reten 425.

## Regenerable Filters

Regenerable filters or back-flushing filters generally comprise a cone-shaped filter media inside a cylindrical housing. The filtration, as opposed to a crossflow filtering or ultrafiltering system, does not use a recirculating feed but relies on 100% transport of the feed through the filter. Back flushing can be done either by timed sequence or by pressure differential across the filter (indicating excessive plugging and low flow).

According to the assessment of Albany Engineered Systems, manufacturers of the Broughton line of regenerable filters, operation of a system such as we propose, with the relatively high level of suspended solids, would require as much if not more water for back flushing than could be recovered during filtration. For this reason regenerable filtration was not given further consideration in this program.

## Pressure Filtration

Direct filtration techniques such as multifiltration, centrifuging, etc., do not seem particularly promising for this program. The high suspended solids content of the water after flocculation (i.e., approximately 1200 ppm) would necessitate fairly frequent replacement of filter media. We gave pressure filtration a brief evaluation to see if there would be a problem with excessive flux decline and filter cake buildup.

We used a Millipore pressure filter funnel (0.0123 $ft^2$ active surface area) to simulate a filter press. The funnel was in turn connected to a 20 inch long, 2 inch diameter stainless pipe which provided a 1-liter capacity for the system. The pipe was loaded from the top with nitrogen pressure.

The filter media was a submicron material designated Grade 5 asbestos fiber filter pad (Ertel Engineering, Inc.).

We used Olive Leaf Soap based wash water (5 liters) which had been coagulated and flocculated with 170 ppm ferric chloride and 0.25 ppm Reten 425.

The filtering was done by filling the stainless steel pipe with pretreated water, capping, and pressurizing to 10 psig. Water flow through the filter was monitored with graduated cylinders and a stopwatch. When the filter ran dry, it was opened and refilled; this was repeated until the water was exhausted.

The results of the filtrations are listed in Table 15. Trials were run using single and double thicknesses of filter media. Actual soap contents (single

filter) were determined by the chloroform/IR analysis technique and reflect accurate results, consistently over 95% soap removal. The apparent soap contents (double filter) were determined by the UV/methylene blue complex method and are probably somewhat in error (falsely low).

The filtration results, particularly with a single filter, are quite promising. The flux rates are very high, despite substantial decline with time. On a proportionate basis, a 1 square foot filter would have filtered approximately 75 gallons of water over the same time period - enough to handle nearly one month's shower water needs in space, presuming a five-man crew and a five-gallon per day water requirement.

The final filter cake thickness was only 5/16 inch. During the filtration we noted that there was a slight recovery in water flux after the filter was emptied, presumably due to partial drying and cracking of the filter cake. It is likely that use of a filter aid such as diatomaceous earth would also tend to prevent flux decline with time.

The energy requirements for such a filtration technique should be quite low since all that is required is a static load. Most other techniques (e.g., centrifuge, ultrafilter, etc.) require moving parts which expend energy (i.e., pumps, motors, etc.).

TABLE 15

Pressure Filtration(1) of Precipitated Wash Water

| Test Duration (min.) | Single Filter | | | Double Filter | | |
|---|---|---|---|---|---|---|
| | Flow ($gf^2d$) | Actual Soap Content (ppm)(IR) | Actual Percent Soap Removed | Flow ($gf^2d$) | Apparent Soap Content (ppm) (UV) | Apparent Percent Soap Removed |
| 2 | 5270 | 45 | 95.5 | 6200 | 79 | 92.1 |
| 6 | 5580 | 42 | 95.8 | 2480 | 72 | 92.8 |
| 12 | 3260 | 43 | 95.7 | 1240 | 83 | 91.7 |
| 30 | 2200 | 43 | 95.7 | 810 | 70 | 93.0 |
| 70 | - | - | - | 650 | 78 | 92.2 |
| 100 | - | - | - | 840 | - | - |
| 120 | - | - | - | 710 | - | - |

(1) Filter media - Grade 5 fiber filter pad
Filter area - 0.0123 $ft^2$
Pressure - 10 psig

## Adsorption with Activated Charcoal

It is likely that activated charcoal will have to be used as a post-treatment step to further reduce the level of organics, particularly surfactant, in the wash water following coagulation and filtration.

Activated charcoal can be employed in two ways. It can be slurried in powder form with the water and then filtered out; or it can be packed in a column in granular form and used to remove organics by slow percolation through the column. We gave preliminary evaluation to both techniques.

1. Slurry Adsorption

The procedure for slurry adsorption was:

- Granular Nuchar WV-G charcoal was pulverized in a mortar and pestle and sieved through a 100-mesh screen.
- Into four clean half-pint jars we placed 0.05 gram each of the 100-mesh charcoal.
- A 500 ml aliquot of Olive Leaf Soap based wash water was coagulated and flocculated using 170 ppm $FeCl_3$ and 0.25 ppm Reten 425, and was filtered through No. 1 Whatman filter paper.
- One hundred milliliter aliquots of the pretreated wash water were adjusted to pH 4, 6, 8, and 10 using dilute NaOH.
- Each aliquot was added to a half-pint jar with charcoal and was agitated for 4 hours in a shaker bath.
- The slurries were filtered through No. 42 Whatman paper and analyzed for apparent soap content by the UV/methylene blue complex technique.

The results were:

| pH | Residual Soap (ppm) |
|---|---|
| 4 | 42 |
| 6 | 55 |
| 8 | 76.5 |
| 10 | 65 |
| Control | 108 |

Although absolute results are somewhat in error due to pH sensitivity and ferric chloride interference of the soap analysis, the trend in the data indicates that Olive Leaf Soap when in the acid form is more easily adsorbed by the charcoal.

2. Column Adsorption

For this work a 2 foot long, 0.7 inch OD glass tube was drawn down at one end to 0.3 inch and was fitted with a piece of rubber tubing, a hose clamp to control flow, and a capillary. A piece of glass wool was placed at the bottom of the column to prevent granules from entering the capillary.

To the column we added 50 grams of Nuchar WV-G granular charcoal (West Virginia Pulp and Paper) in water slurry. The column was back flushed through the capillary to remove trapped fines and air bubbles.

The wash water was first pretreated by coagulating and flocculating with 170 ppm $FeCl_3$ and filtering through No. 1 Whatman paper. This pretreated water, pH 3.2, was allowed to flow through the charcoal column at 3-4 cc per minute (approximately 20 minutes residence time). Samples were collected at 100 ml intervals. Residual soap levels for all aliquots were at an undetectable level, indicating a residual level probably less than 1 part per million.

Initial soap level of the pretreated and filtered wash water was 39 ppm. Therefore it appears that adsorption with activated charcoal is a promising technique for removing trace soap from pretreated wash water.

## V. OPERATIONAL PARAMETERS AND DESIGN CRITERIA

As a result of the concept development, we have found techniques which appear suitable for the development of a pretreatment system for removing soap from wash water. A pretreatment system might consist of the following:

1. A hold tank for storage of shower water (probably 5 to 10 gallon capacity).

2. A mixing tank for chemical precipitation of the soap from the water. A tank of 5 to 10 gallon capacity would be adequate. Since the mixing would be done only intermittently, one tank would serve for both rapid and slow mixing (i.e., 100 rpm and 30 rpm). The tank would be equipped with a paddle-type stirrer.

3. A small hold tank would be necessary for ferric chloride solution. If a 40% solution were used (Dow Chemical sells such a solution), a 1-gallon tank would be adequate for a year's supply of coagulant.

4. A metering pump would be necessary to deliver the desired dosage of ferric chloride to the mixing tank. Optimum dosage, assuming an Olive Leaf Soap based wash water, would be 170 ppm.

5. The coagulated water would then be pumped to either a cross-flow filtration loop or a pressure filter; due to simplicity and low energy requirement, a pressure filter seems more feasible.

   The filter reservoir would probably be expandable (i.e., bellows or diaphragm) and would be loaded from the top with nitrogen pressure, which would force the water through the filter media.

6. The filtered water would be pumped through an activated charcoal column to remove trace organics.

7. Before the RO step, the pretreated water will likely be adjusted to neutral pH (ferric chloride coagulation leaves the water at a pH of between 3 and 4).

We feel that development of specific design criteria and system parameters would be premature at this time for the following reasons:

1. No specific recommendation has been made by NASA as to a personal hygiene cleansing agent. Several surfactants are under consideration, including Neutrogena, Miranol JEM, and Olive Leaf Soap. The decision as to which agent will be used for space flight will involve consideration of dermatological effects, foaming characteristics, effectiveness as a cleansing agent, acceptability by the crew, and possibly the ability to be removed by pretreatment techniques.

   Unfortunately, it is impossible to be sure at this time that any cleansing agent selected by NASA will be capable of removal by a ferric chloride precipitation/filtration/activated charcoal type system.

2. No specific recommendation has been made by NASA regarding an RO membrane type and configuration. Several membranes are under consideration, including CA blend, sulfonated PPO, polybenzimidazole (PBI), and the new NS-100 (toluene diisocyanate/polyethylenimine condensate polymer). In general, hollow fiber and tube membranes are more compact (greater water flux per cubic foot of desalinating module), but flat membranes often perform better, yielding higher water flux and superior salt rejection.

   Once a membrane and configuration have been selected by NASA, it will be necessary to determine that membrane's tolerance to cleansing agent or agents and other contaminants (suspended matter and dissolved organics). The results, depending on the membrane, could range from no pretreatment necessary up to the necessity to remove every trace of organics. Depending on the membrane/soap combination, it is possible that:

   a. Only chemical pretreatment, no charcoal adsorbent, would be required.

   b. Simple prefiltration would be all that would be required.

   c. Proper RO system design with good clearance above the membrane and high surface velocity would obviate pretreatment.

It seems premature, therefore, to develop design criteria and operational parameters for a pretreatment system until these tolerances are known.

3. More detailed laboratory study will be required on a given proposed system before design criteria and operational parameters can be detailed. It will be necessary to know such information as pressure tolerances and crossflow velocity tolerances for crossflow filters, life expectancy of activated charcoal adsorbants, life expectancy of filter media, etc.

It is possible at this time, however, to give some general remarks as to design criteria and operating conditions.

Due to the relatively low anticipated water requirements (1 gallon per day each for a five-man crew), the system will run only intermittently - probably once every day or two. Due to the zero-G environment, water will have to be moved by positive displacement pumping and/or pressurized bellows or diaphragms.

Since relatively low pressures will be used (e.g., 10 psig for pressure filtration), small centrifugal pumps can probably be employed for moving water.

To avoid the difficulties of corrosion, polymeric materials would be used in as many areas as possible, particularly for tanks, pump heads, and pipe in contact with concentrated ferric chloride. Polymers would also represent a substantial savings in weight over metal counterparts.

There are numerous types of materials that could be used. For piping, ASTM grade 2308 or 2306 polyethylene pipe could be used; these grades are rated by the Plastic Pipe Institute for 800 psig and 600 psig, respectively, for long-term operation - i.e., these pressures represent one-half that which would be necessary to cause the pipes to fail in an average time span of 100,000 hours or over ten years. Materials for other components might include reinforced composites for propeller blades and shafts; Teflon for bearings; acetal, nylon, Noryl, or polycarbonate for pump components; as well as glass-reinforced polyester, acrylic, polypropylene, ABS, etc., for other noncritical areas.

Maintenance requirements will depend on the need for system element replacement (i.e., filter cartridges or media, and activated charcoal columns). The frequency of replacement will depend on the life expectancy of

these components, which can be determined to some degree by their size or surface area. There will probably be some trade-off between element size and frequency of replacement. It might be advantageous to have several small components connected in parallel rather than have one large unit. One of the elements could be cleaned or replaced without forcing shutdown of the entire system.

More detailed information on such a pretreatment system will have to await decisions as to soap and RO membrane to be used and more exhaustive laboratory studies on system operating parameters.

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